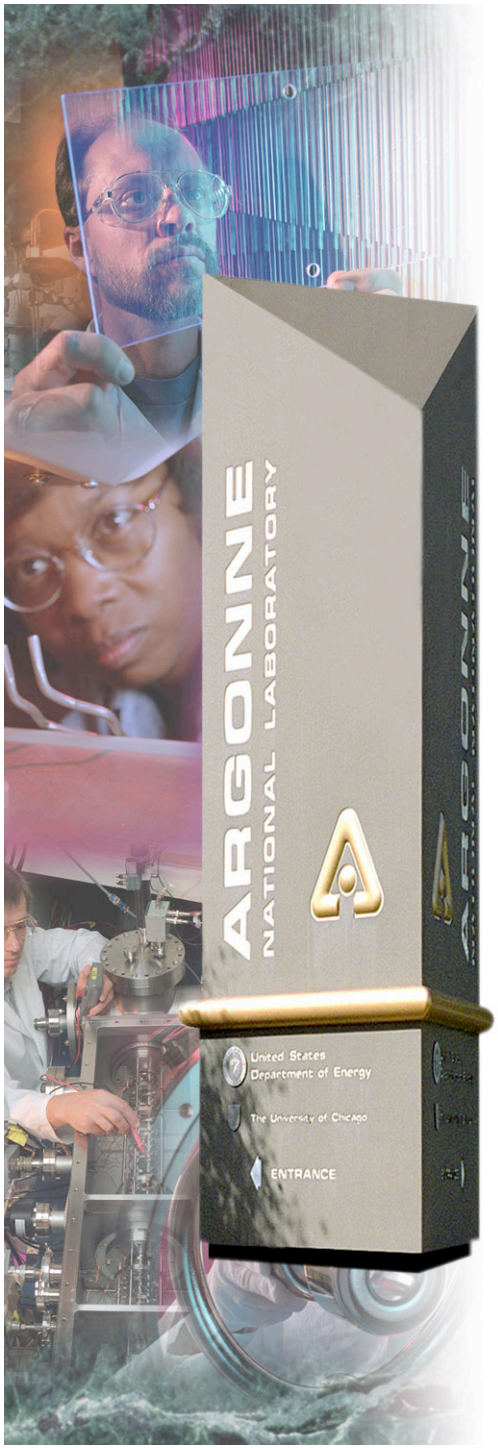

MD simulations of diffusion, sputtering and bubble formation in liquid Li

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Office of Science
U.S. Department of Energy

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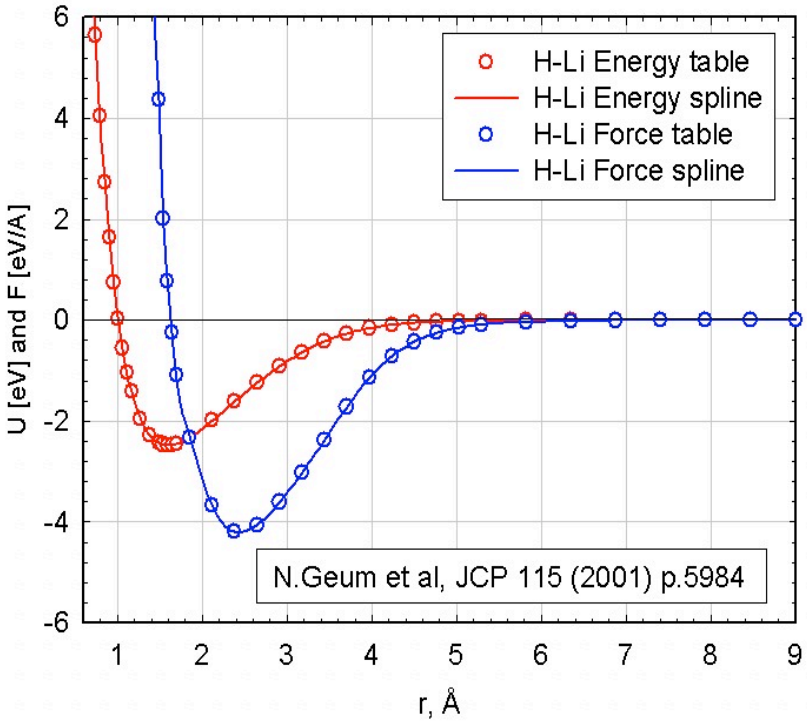
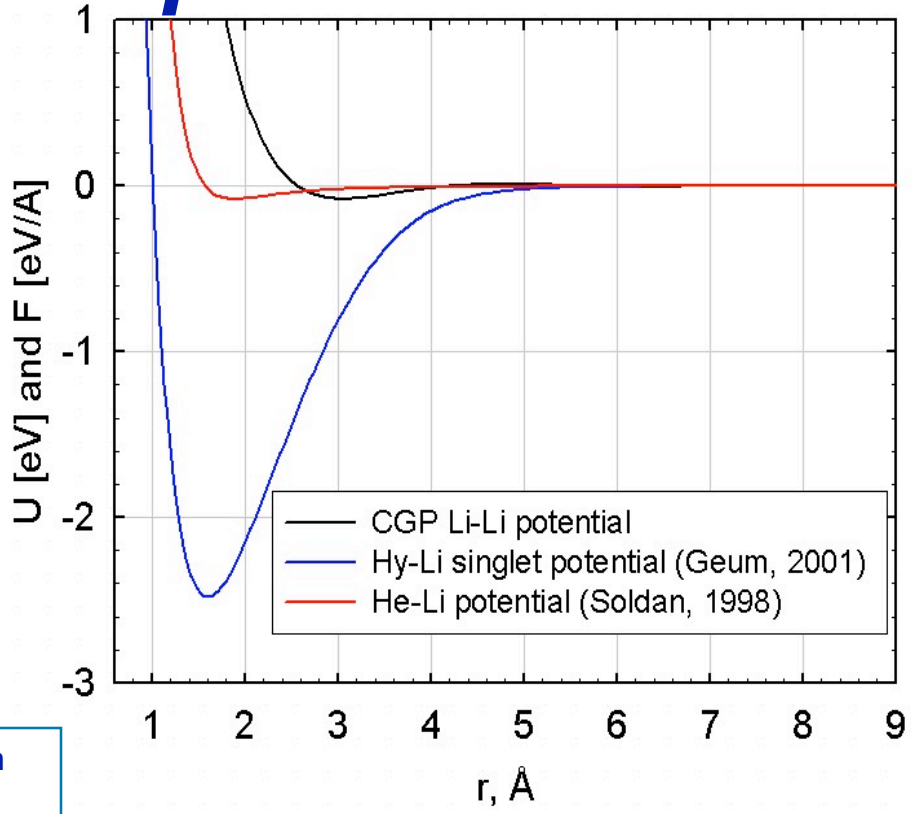
Office of Science Laboratory
Operated by The University of Chicago

Outline

- Introduction – H, Li potentials
- Diffusivity of H,D,T atoms in Lithium
- Sputtering of Li by H, D, T ions
- Bubble formation in liquid Li

H/Li interaction potential





MD method needs accurate interaction potentials between the particles in the system.

Recently, a new H-Li potential was developed by ab-initio calculations of the lowest singlet ^1S and triplet ^3S states for LiH and applied for analysis of trapping of cold atoms in [1].

The singlet form of this H-Li potential (circles - tabulated data) were used for building the energy and force cubic splines (red and blue lines).

[1] N. Geum et al, JCP115 (2001) p.5984

H-Li potential well (blue line) is much deeper than the He-Li (red line) and Li-Li potential (black line).

Analytical EAM-Li-Li potential #1

TB QM (Eq.1) was used in [1] for obtaining a suitable ion-ion potential for disordered Lithium systems (small clusters, surfaces).

$$(\varepsilon_{ia}^{0} - E)\,|ia\rangle + \sum_{j\neq i}\sum_{b} t_{ab}^{ij}(r_{ij})\,|ib\rangle = 0, \quad (1)$$

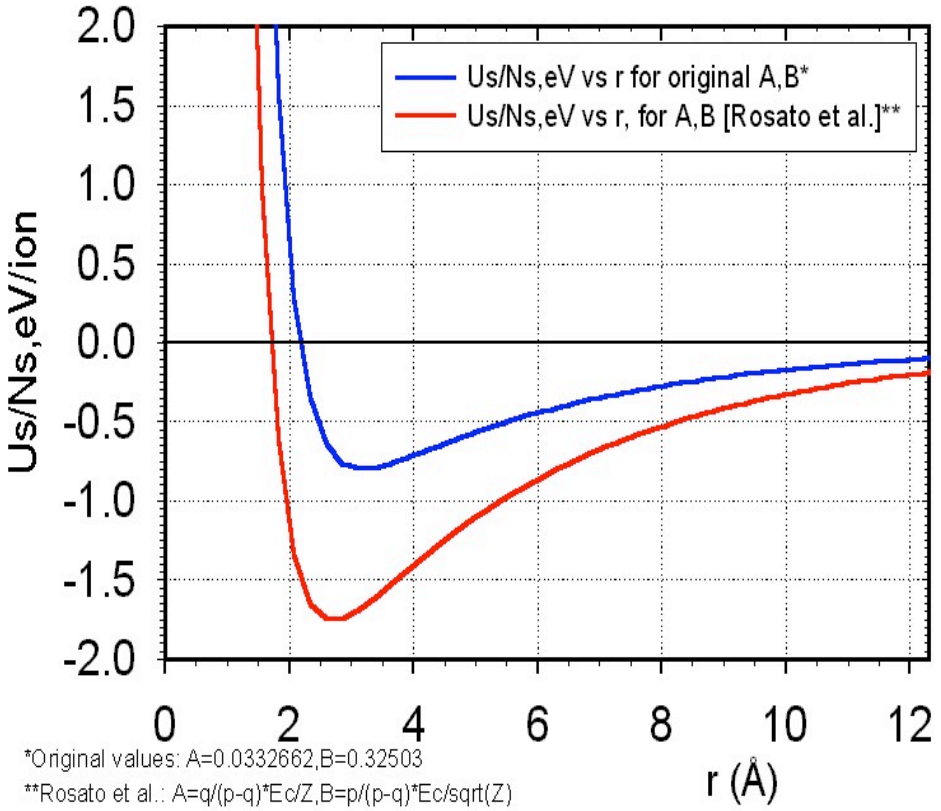
$$U_{\text{coh}} = U_{\text{el}} + U_{\text{rep}},$$

$$U_{\text{rep}} = \sum_{i}\varepsilon_0 \sum_{j\neq i}\exp\left[-p\left(\frac{r_{ij}}{r_0}-1\right)\right],$$

$$U_{\text{el}} = -\sum_{i}\left\{\sum_{j\neq i}\varsigma^{2}{}_0 \exp\left[-2q\left(\frac{r_{ij}}{r_0}-1\right)\right]\right\}^{1/2}$$

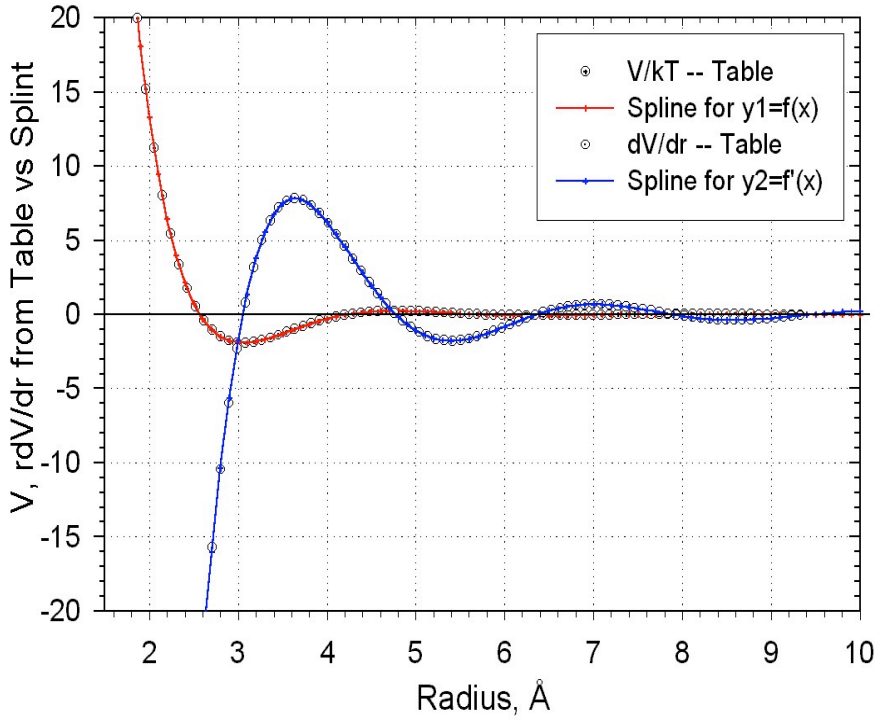
Parameters used for this simulation:

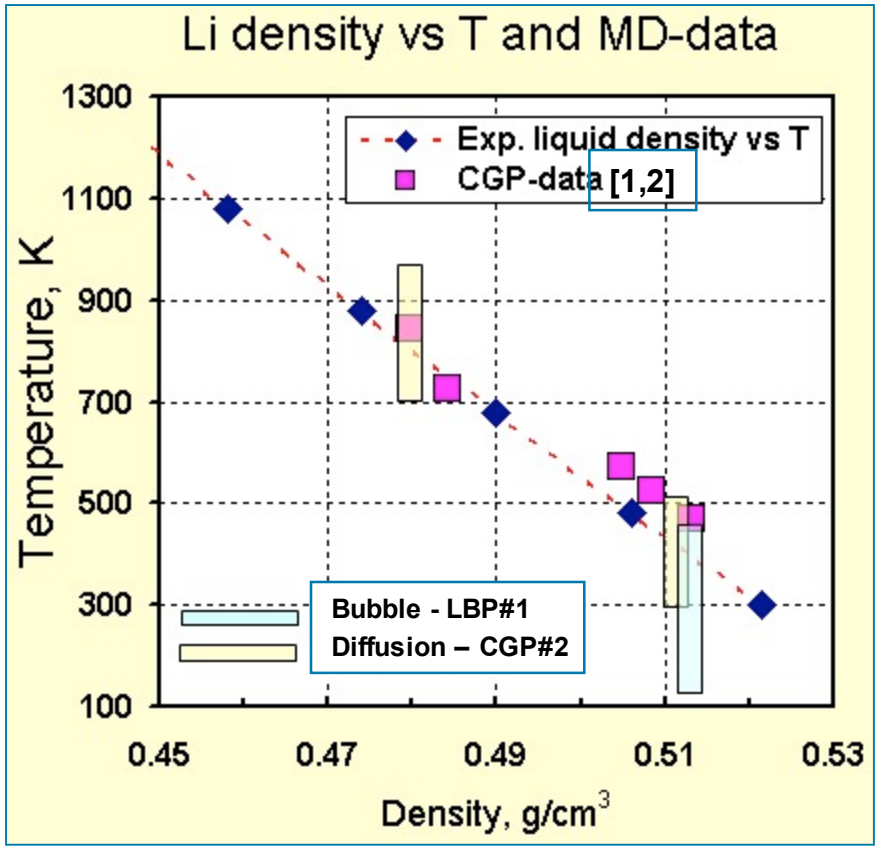
	ε_0, mRy	ς_0, mRy	p	q	r_0, a.u.
Li-Li:	2.4450	23.889	7.75	0.737	5.490



[1] Y. Li et al, Phys. Rev. B57 (1998) 15519

Li-Li bulk interaction potential #2

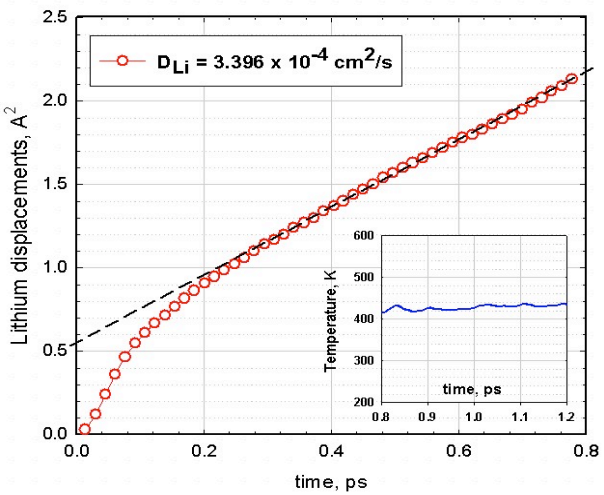


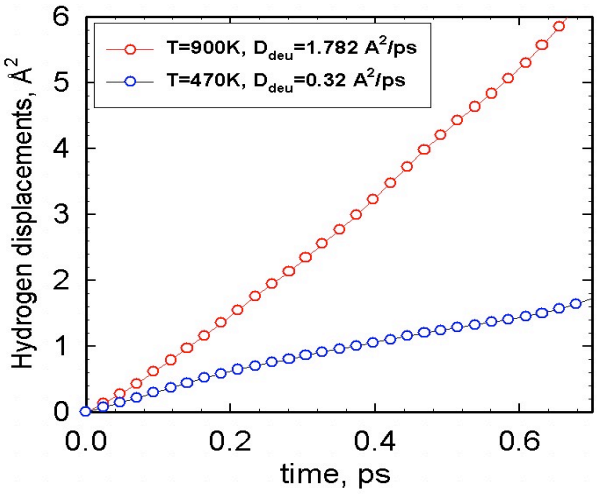


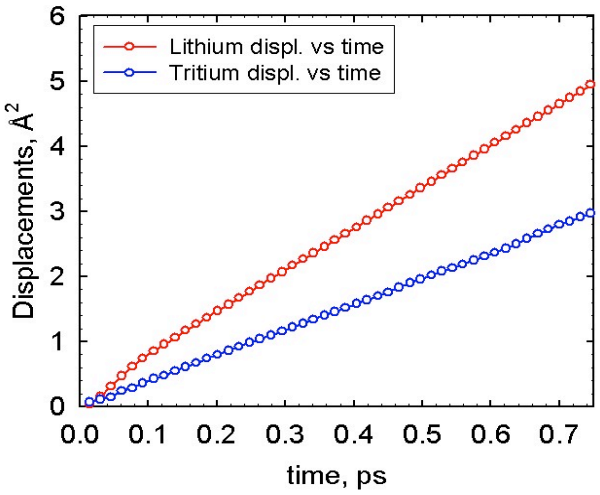
The tabulated Li-Li bulk potential and its first derivative given in [1,2] (circles) and cubic splines (red and blue lines) used in this work.

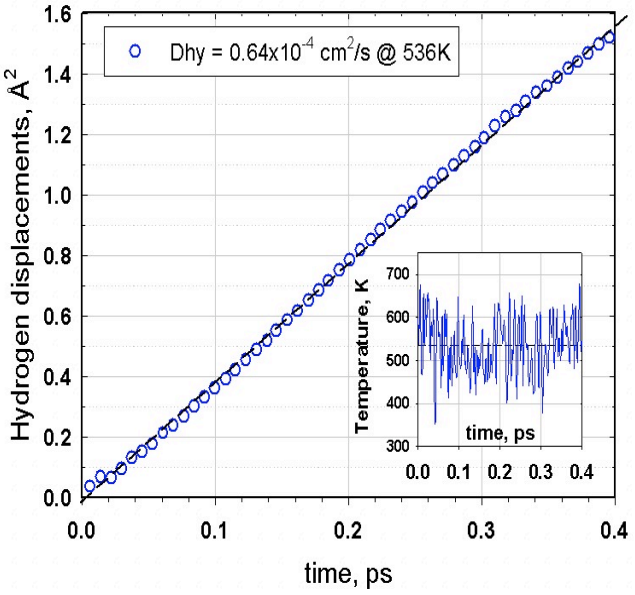
References:
[1] M. Canales et al, J. Phys. 5 (1993) 3095.
[2] M. Canales, Phys.Rev. E50 (1994) 3656.
[3] H. Morimoto et al, NASDA reports, 1999.

Li, H, D, Tr displacements





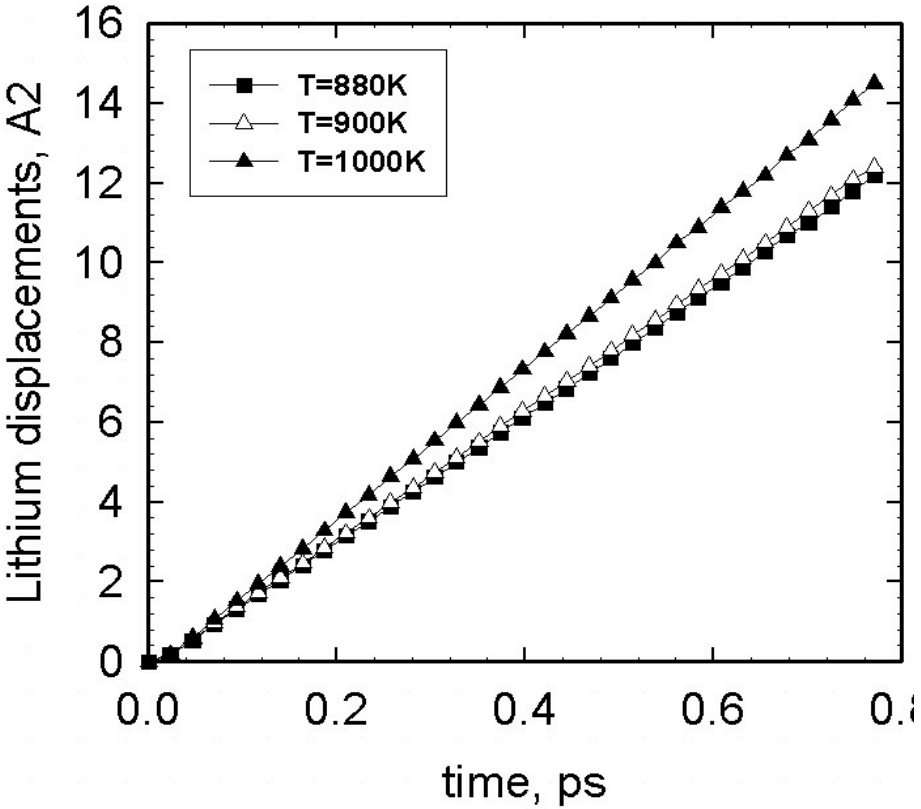


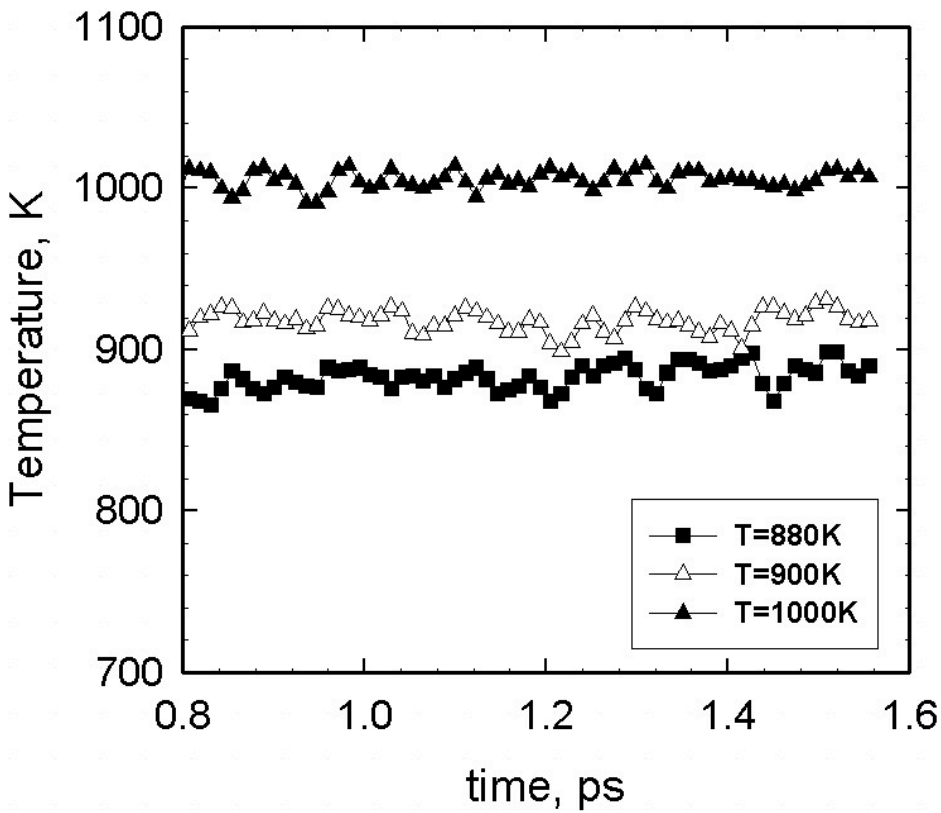


$$\left\langle \Delta r^2(t) \right\rangle = \left\langle \frac{1}{N} \sum_{i=1}^{N} \vec{r}_i(\tau)\vec{r}_i(\tau + t) \right\rangle_{\tau} \qquad (1)$$

Time-dependence of the mean-square-displacements of lithium ions and hydrogen, deuterium and tritium atoms were calculated by (eq.1)at various temperatures and densities of a mixture of Li and H (< 1% concentration in lithium).

Liquid Li displacements

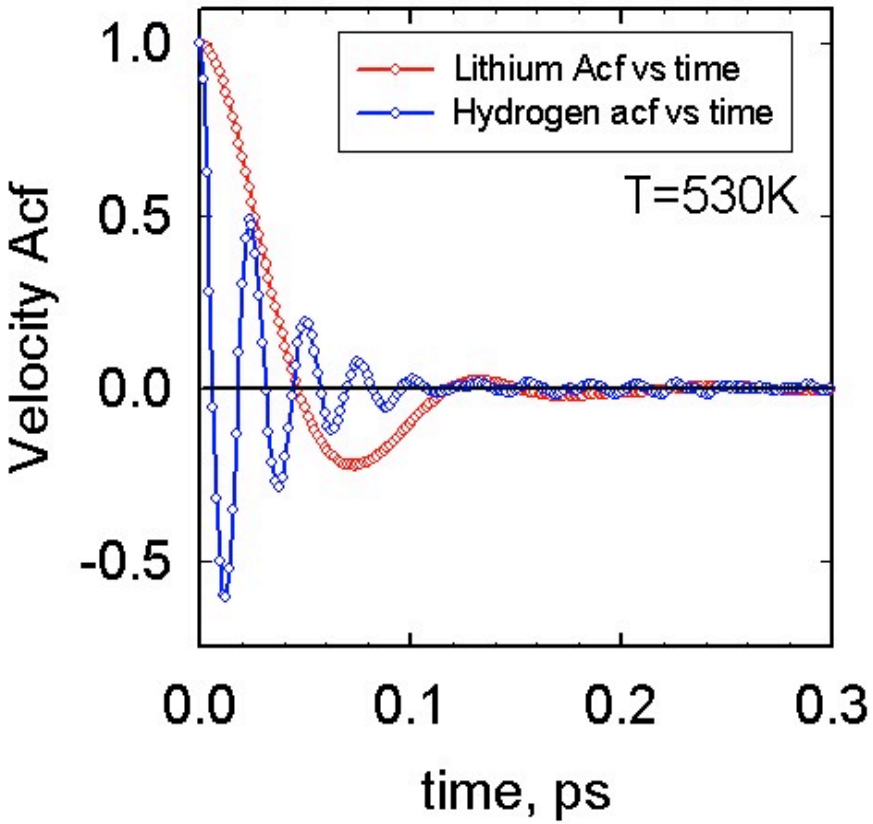


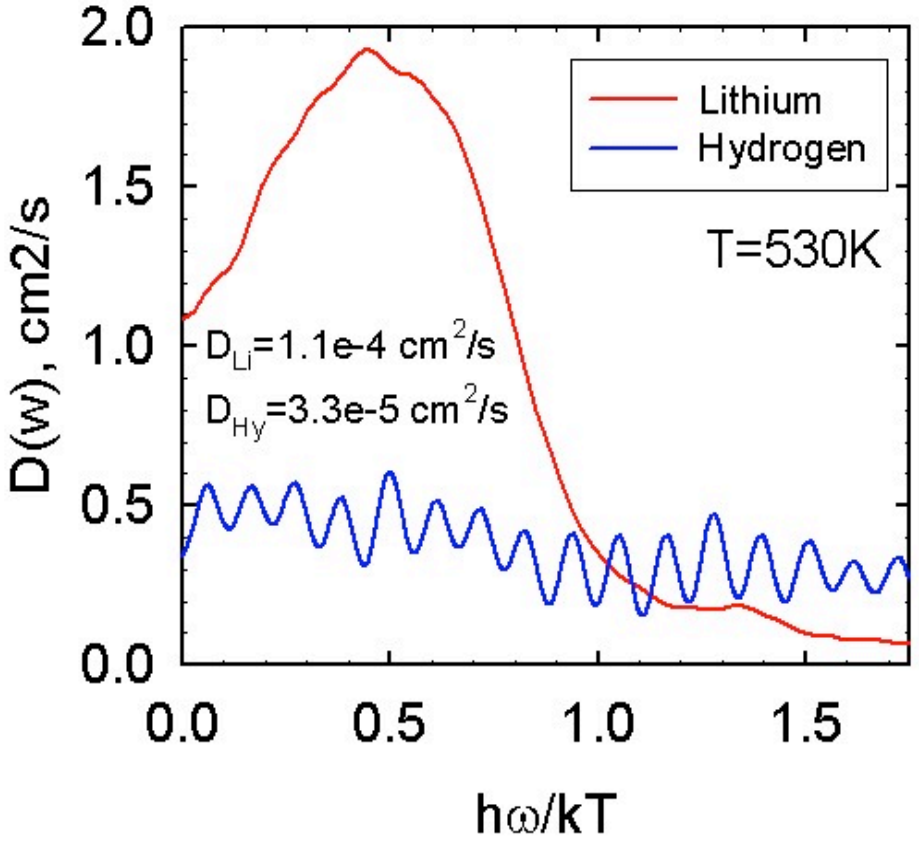


$$(2)\quad D_\alpha = \lim_{t\to\infty} \frac{\left\langle \Delta r_\alpha{}^2(t) \right\rangle}{6t}, \qquad \alpha = Li, H, D, T$$

The diffusion coefficients were obtained by two methods: a) 1st method uses Eq. 2 which obtains diffusion coefficient as a tangent of the linear region of the displacement function; b) The 2nd method consists in calculation of the velocity auto-correlation functions *Acf* (t) and then in obtaining the spectral density *D*(w). The diffusion constants are the values at w=0.

Li, H Acf and diffusivity

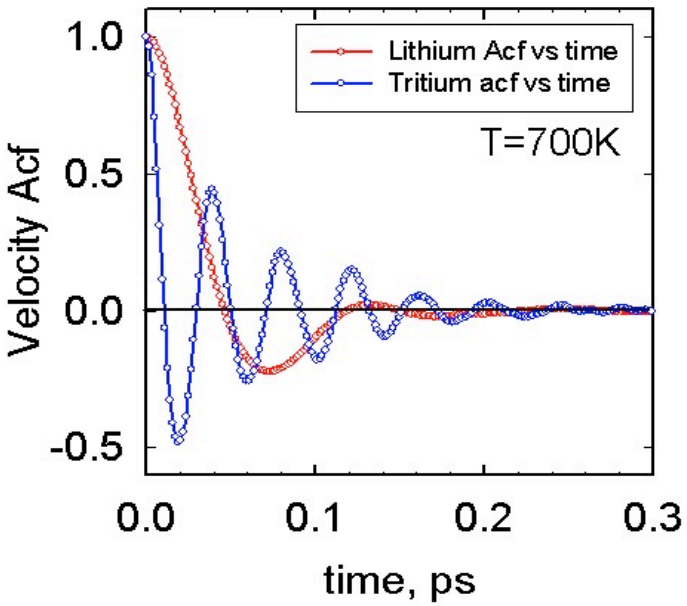


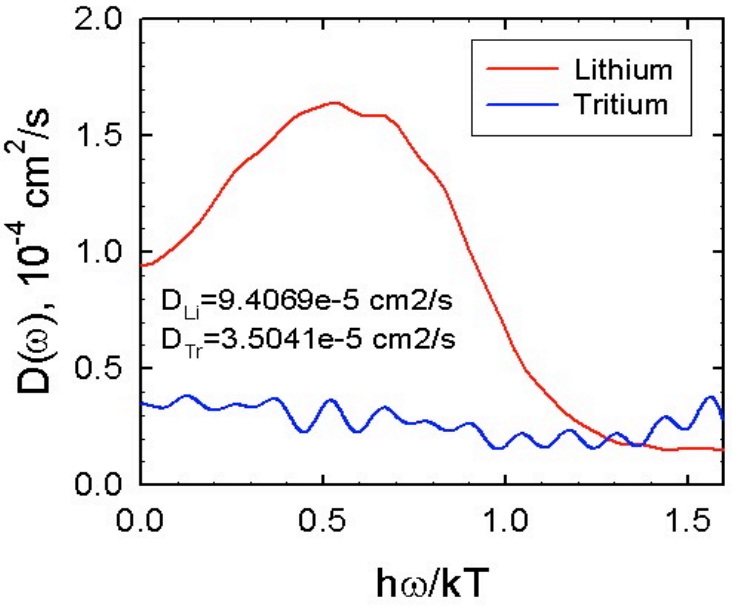


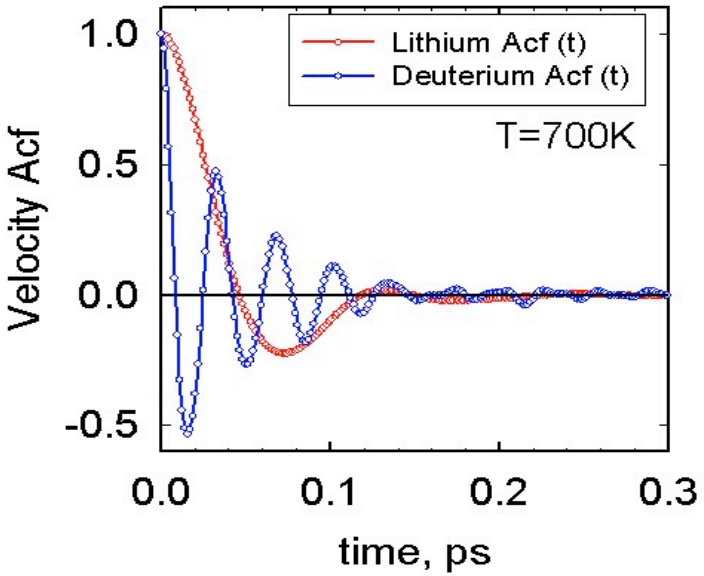
(3) $$Acf(t) = \left(m/3k_BT\right)\sum_{i=1}^{N}\langle \vec{v}_i(0)\vec{v}_i(t)\rangle_\tau$$

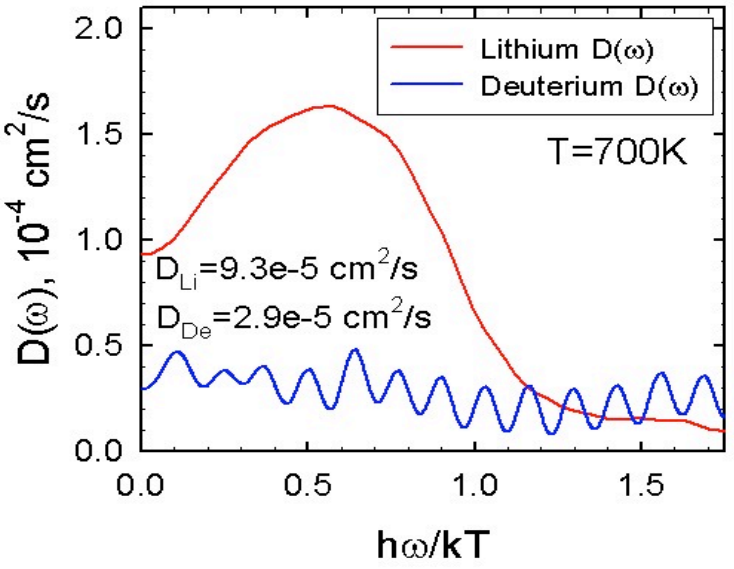
(4) $$D(\omega) = \left(k_BT/m\right)\int_0^\infty Acf(t)\cos(\omega t)dt$$

D, Tr, Li acf and diffusivities

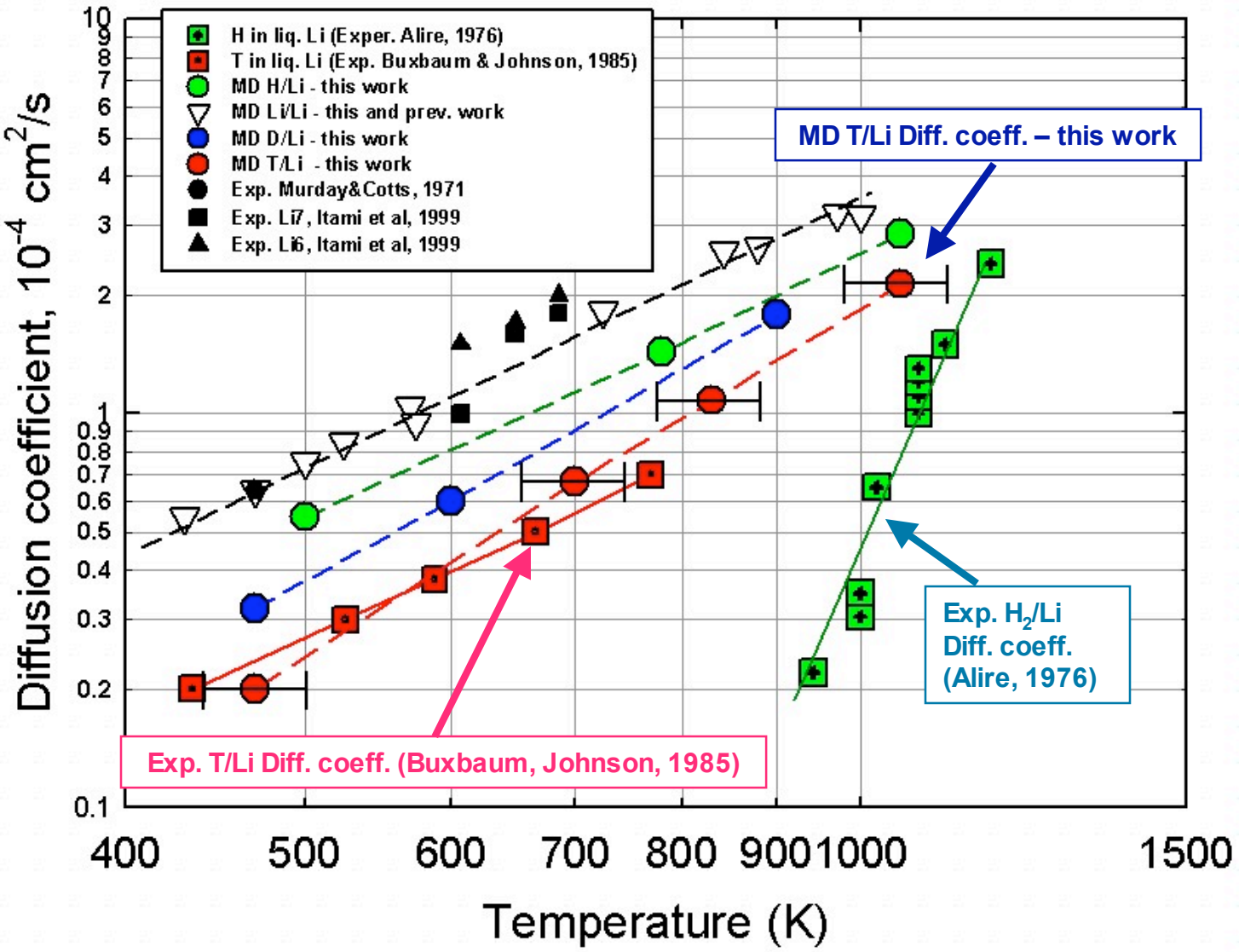




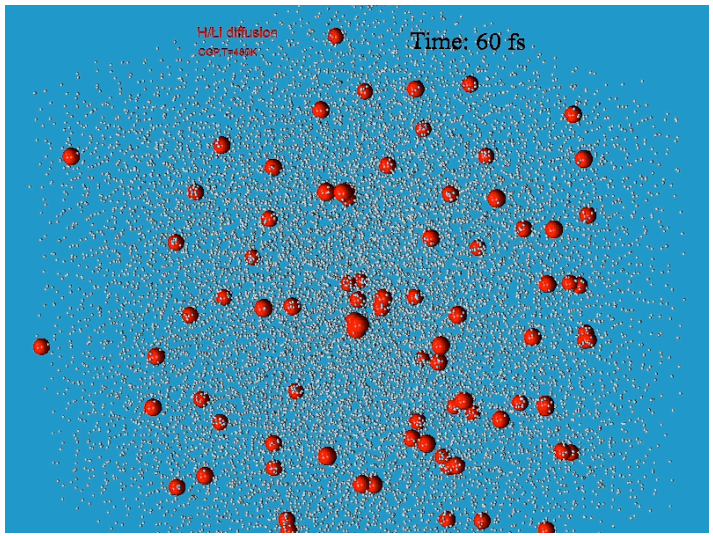


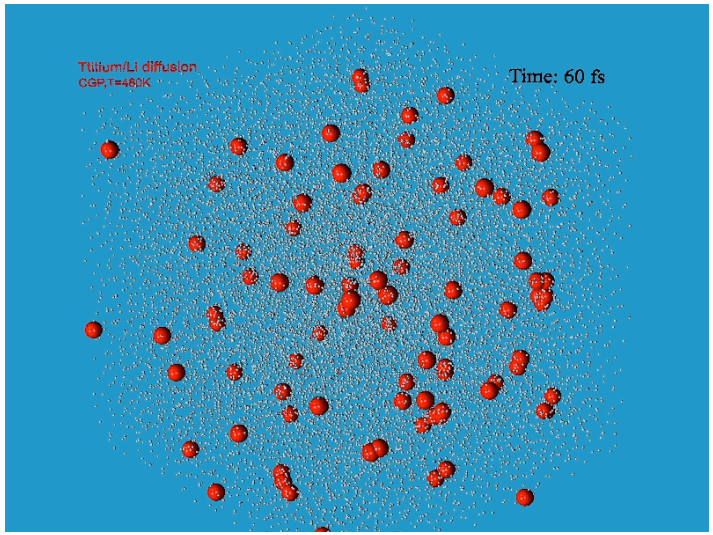


Diffusivity of H, D, Tr in liquid Li

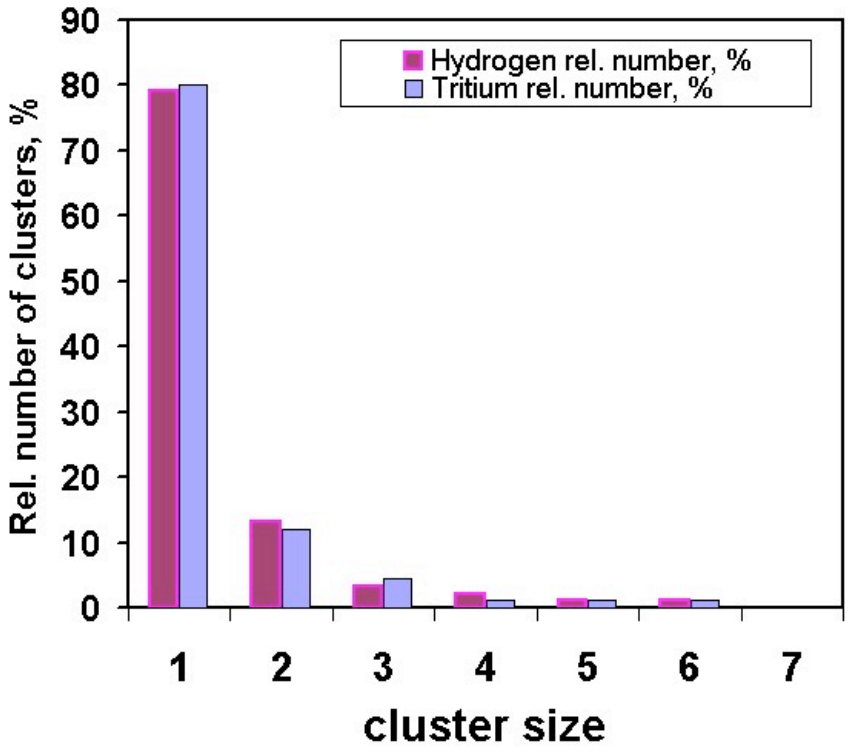


Hydrogen cluster formation in liquid Li

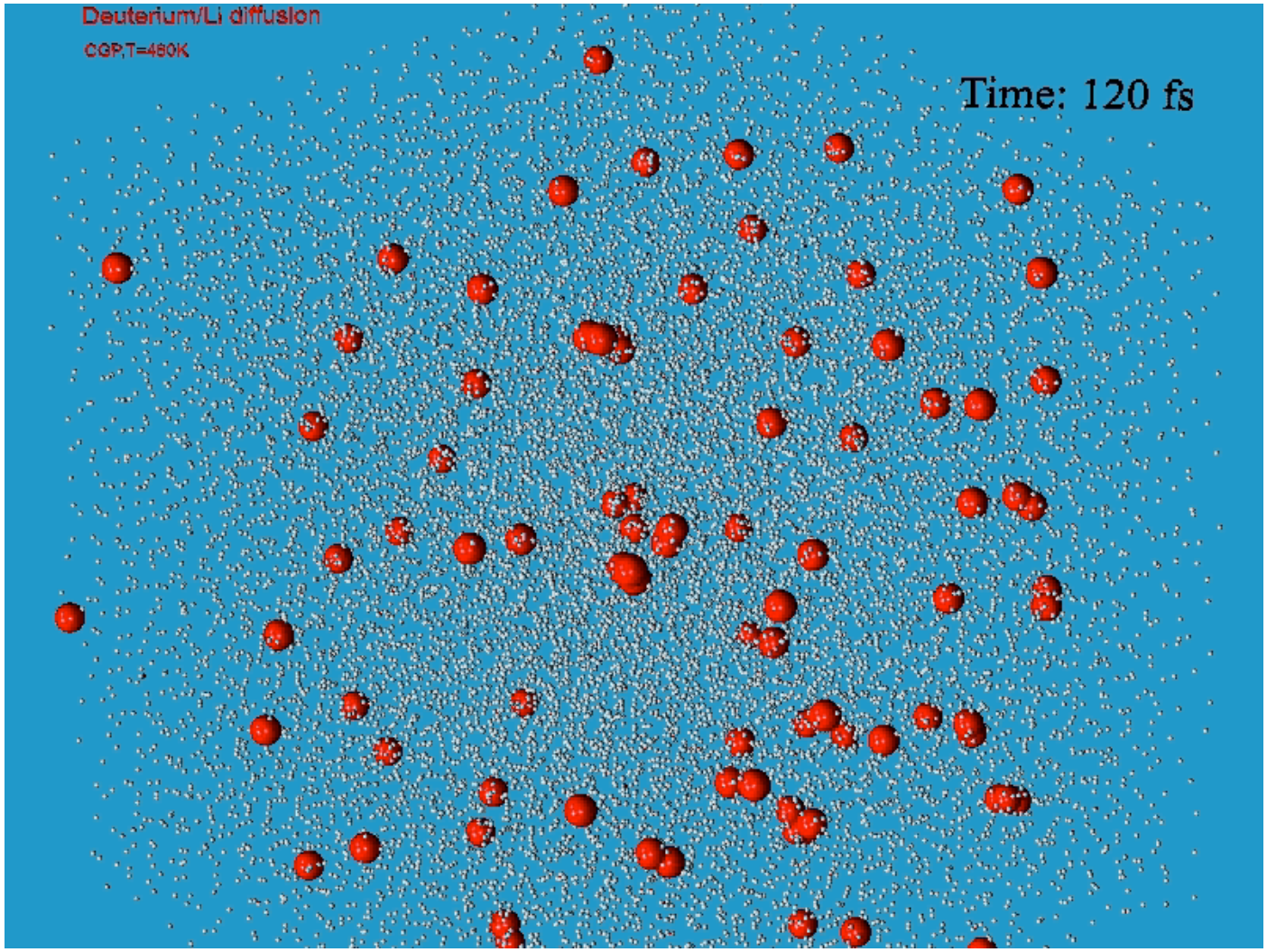




n	1	2	3	4	5	6	7
Nn (Hydrogen)	72	12	3	2	1	1	0
Relative number of Hn, %	79.1	13.2	3.3	2.2	1.1	1.1	0
Nn (Tritium)	73	11	4	1	1	1	0
Relative number of Trn, %	80.2	12.1	4.4	1.1	1.1	1.1	0



Deuterium clusters in liquid Li @ 480K



Summary #1

- The H-Li potential was tested by calculating the diffusion coefficients of Hydrogen isotopes in liquid Li at various temperatures and densities.
- The calculated tritium diffusion coefficient in liquid Lithium is in good agreement with the experimental results of Buxbaum & Johnson (1985).
- A noticeable amount of hydrogen clusters in liquid Li (>10%) is obtained by this MD study. These clusters are still highly mobile.
- Future MD tasks: a) Temperature stabilization during cluster formation; b) The kinetics of Hn cluster formation could be studied by direct MD.

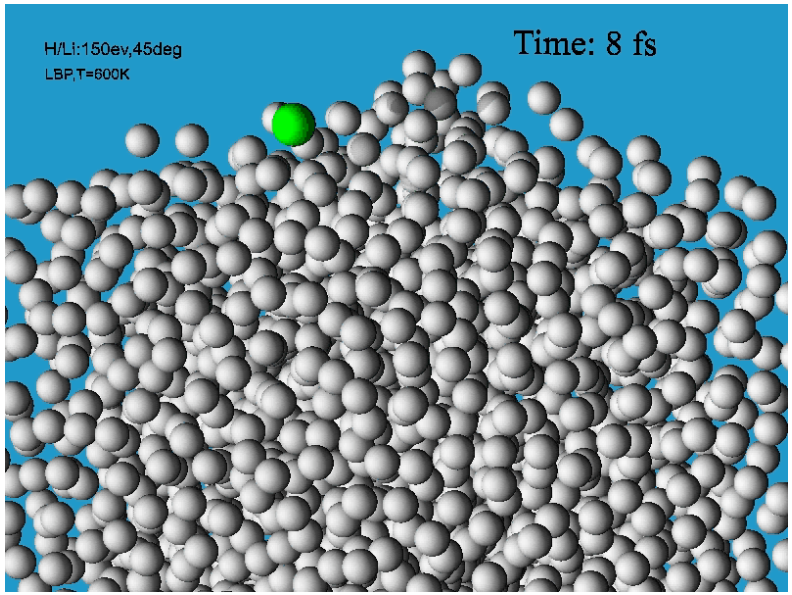
Outline

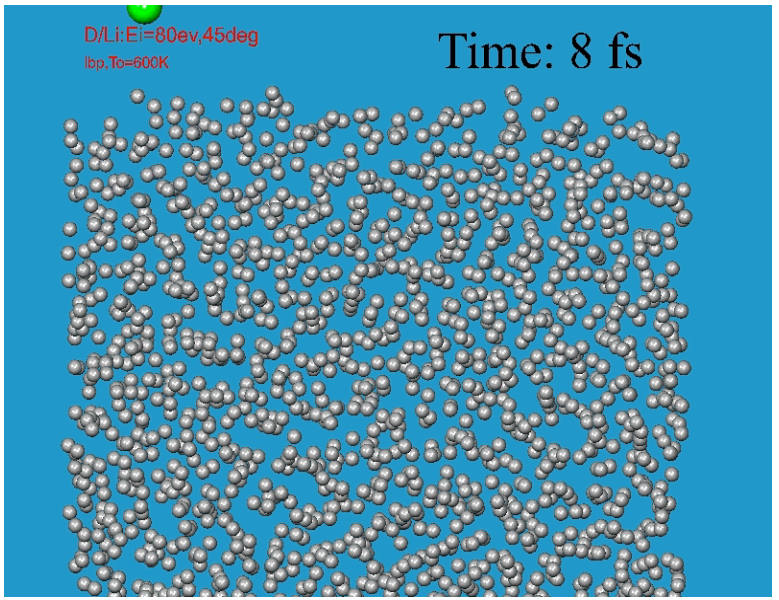
- Diffusivity of H, D, T atoms in liquid Lithium
- **Sputtering of Li by H,D,T ions**
- Bubble formation in liquid Li

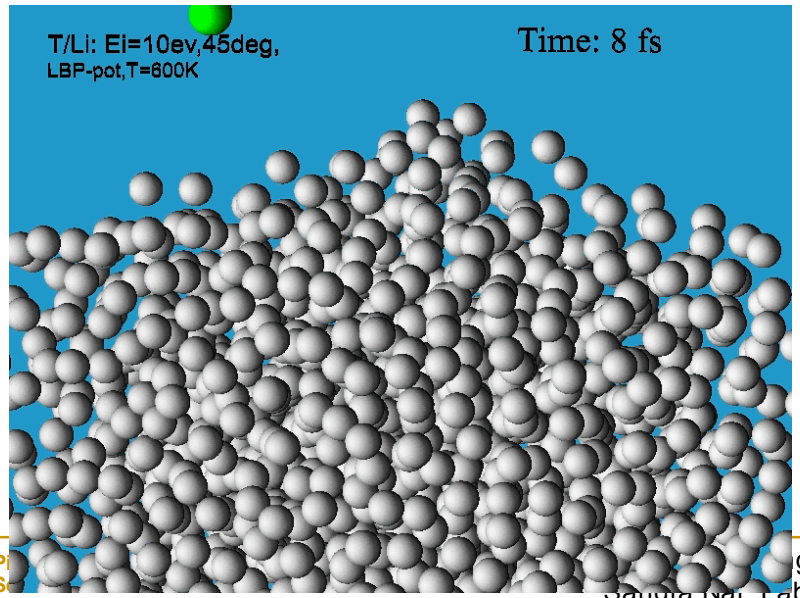
Sputtering simulation model

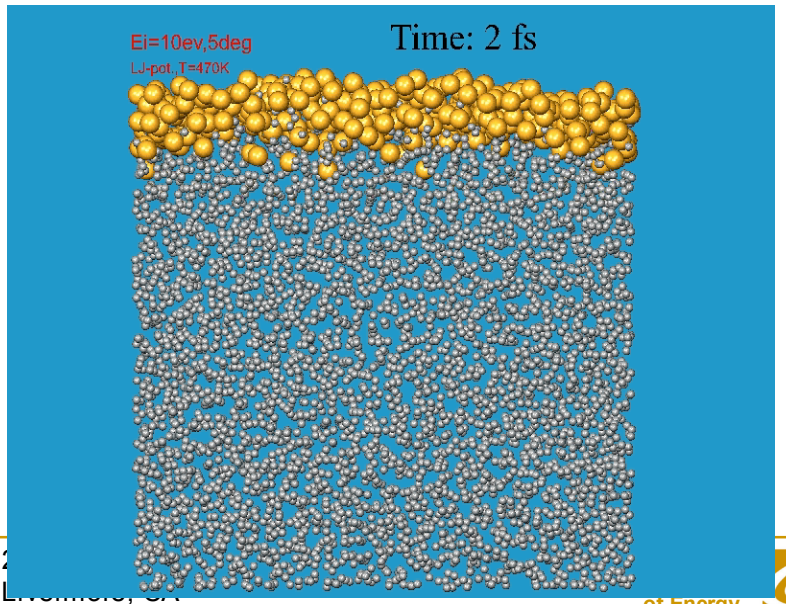
- The singlet-type H-Li potential given by Geum et al, 2001 was used for simulation of H,D, and T collisions with a lithium surface.
- Lithium surface was modeled by various types of Li-Li potentials.
- Image forces were added to the interaction between Hydrogen ions with the liquid Lithium surface.
- Sputtering yield, reflection and sticking coefficients, energies etc. were calculated for a wide range of temperatures and ion energies in the interval of 10 – 300 eV.

H-Li collision movies

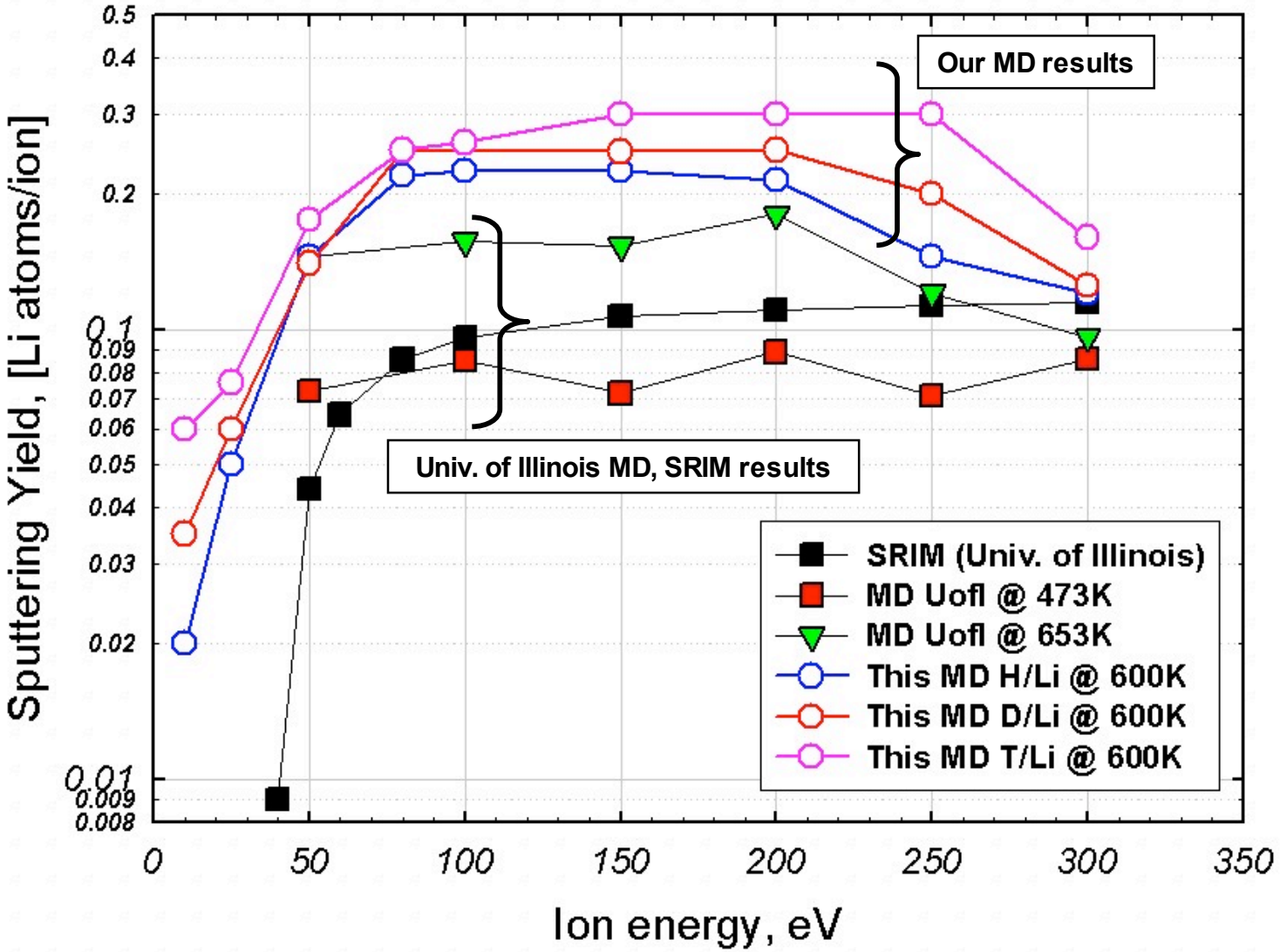




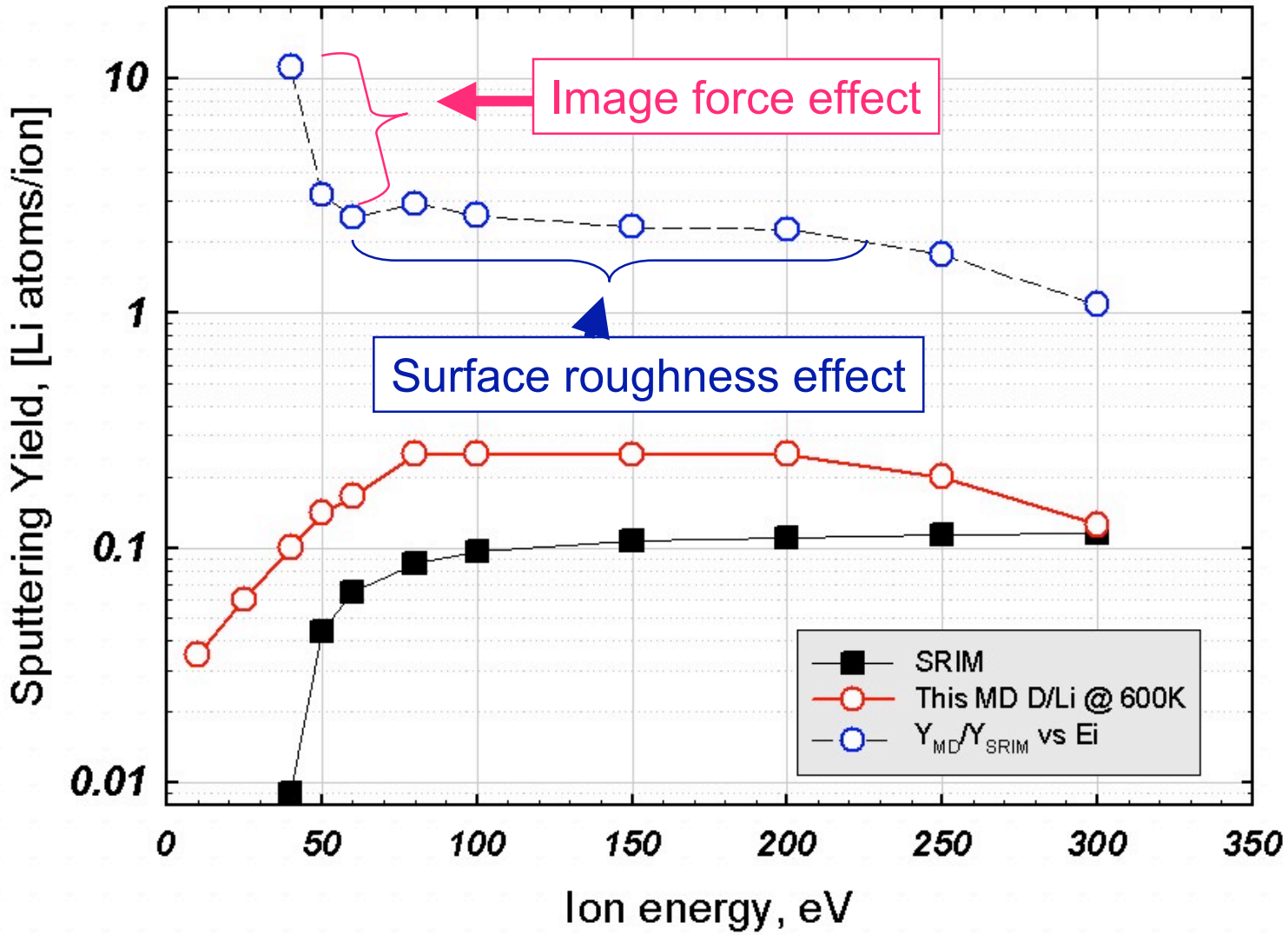




Sputtering yields of Li surface with H, D, Tr ions



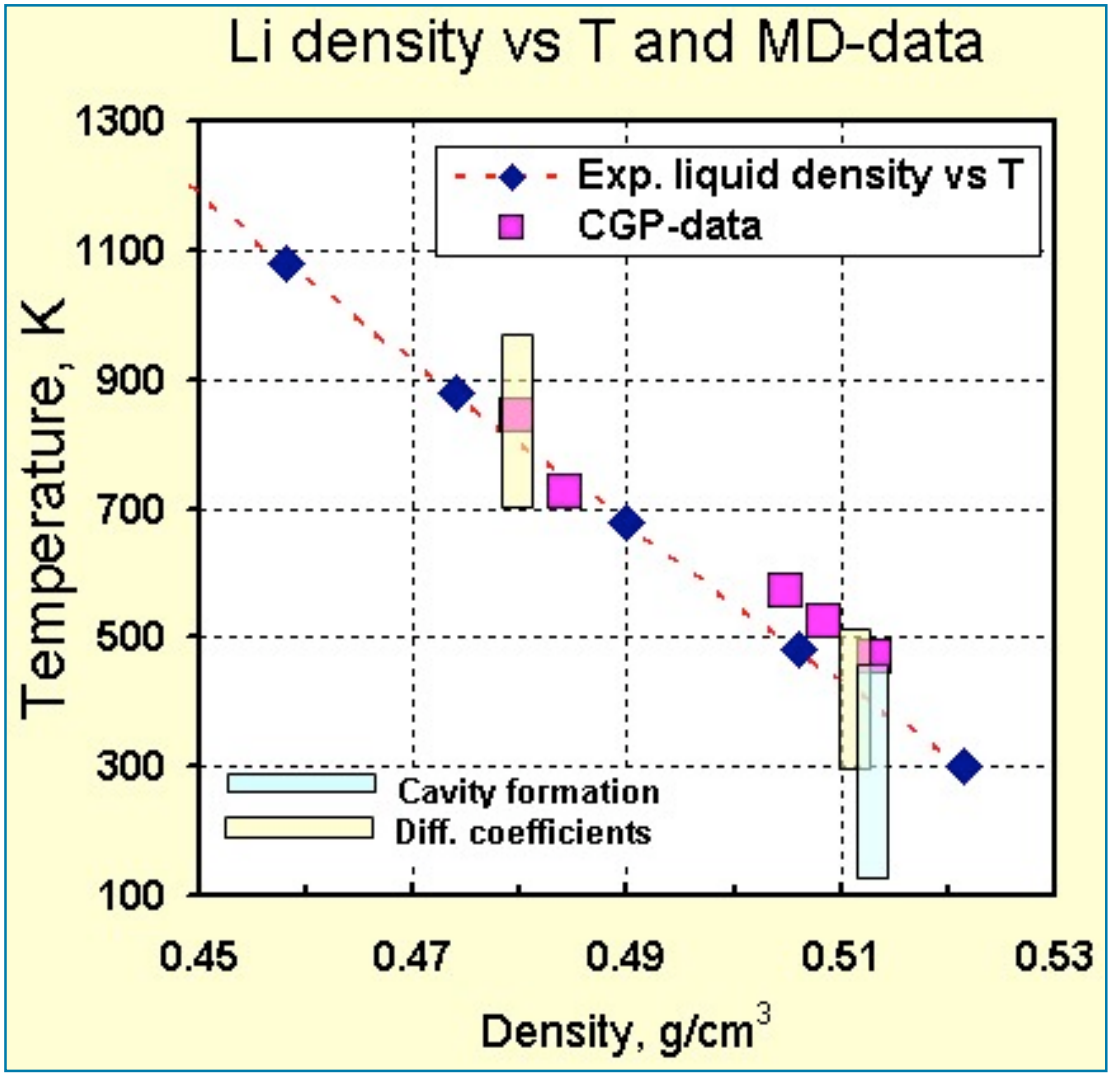
Comparison of D/Li sputt. yields: MD vs SRIM

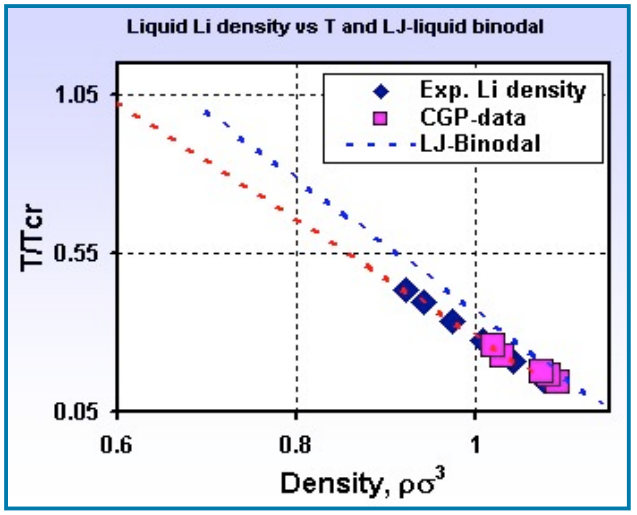


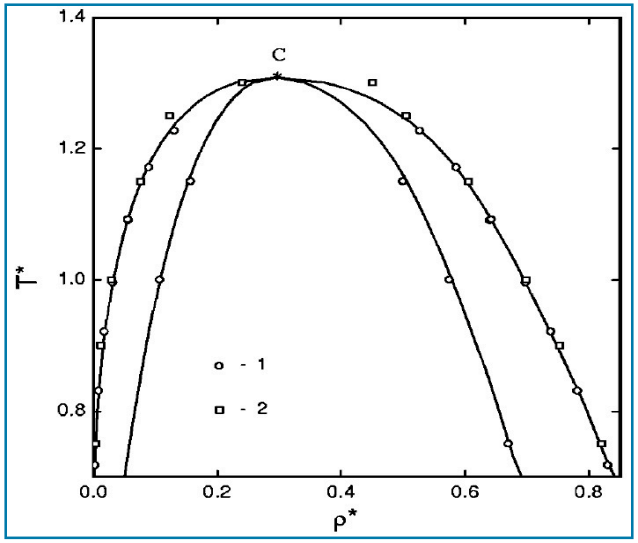
Outline

- Diffusion coefficients of H, D, T in liquid Lithium
- Sputtering Yields of H, D, T on a Li surface
- **Bubble formation in liquid Li**

Liquid Li density vs Temperature







Surface tension and free energy of a cavity

The Tolman's formula

$$\gamma_S / \gamma_\infty = 1 - \frac{2\delta}{R_S},$$

$$\delta = R_e - R_S$$

g_S – Bubble surface tension,

g_∞ – plane surface tension,

***R*e, *R*s – radii for the equimolar surface and the surface of tension**

$$\Delta \dot{U}(r) = -\frac{4}{3}\pi r^3 \cdot \Delta\omega + 4\pi r^2 \cdot \gamma_S,$$

$$\Delta\omega = P_g - P_l$$

$$\frac{d\Delta\Omega}{dr} = 0 \Rightarrow \Delta P = \frac{2\gamma_S}{R_S} \text{(Laplace eq.)}$$

$$R_S = \frac{2\gamma_S}{P_l - P_g},$$

$$R_e = \frac{1}{\rho_l - \rho_g}\int_0^\infty r^3 \frac{d\rho}{dr} dr.$$

We obtained radial pressures around a bubble in liquid in analogy with the droplet capillary theory [1,2]. Bubbles in a LJ-system were studied by MD in [3].

References

[1] Thompson, Gubbins et al, JCP, 1984

[2] Lee, Telo da Gama, Gubbins, JCP, 1986

[3] Park, Weng, Tien, Int. J. Heat & Mass Transfer, 12001

MD calculation of variables

$$P(r) = P_N(r) + P_{Tr}(r),$$

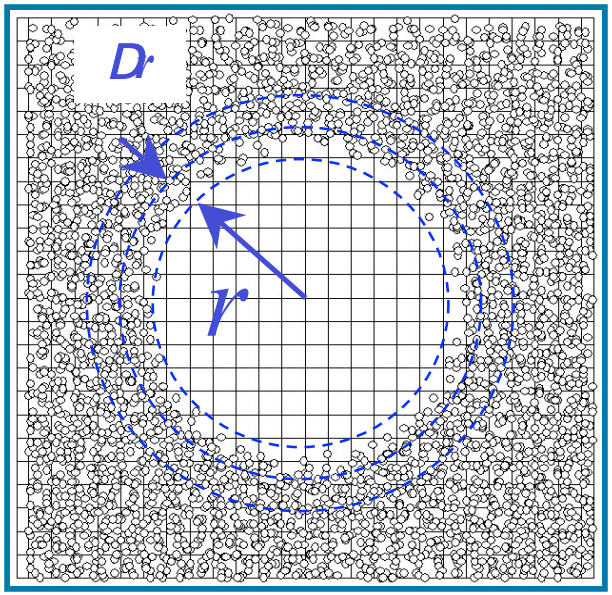
$$P_T(r) = P_N(r) + \frac{r}{2}\frac{dP_N(r)}{dr},$$

$$P_N(r) = P_{Kin}(r) + P_U(r),$$

$$P_{Kin}(r) = \rho(r) k_B T,$$

$$P_U(r) = -\frac{1}{4\pi r}\sum_k \left|\vec{r}\cdot\vec{r}_{ij}\right|\frac{1}{r_{ij}}\frac{dU(r_{ij})}{dr_{ij}},$$

$$\gamma_S^3 = -\frac{1}{8}(P_l - P_g)\int_0^\infty r^3 \frac{dP_N}{dr}\,dr.$$

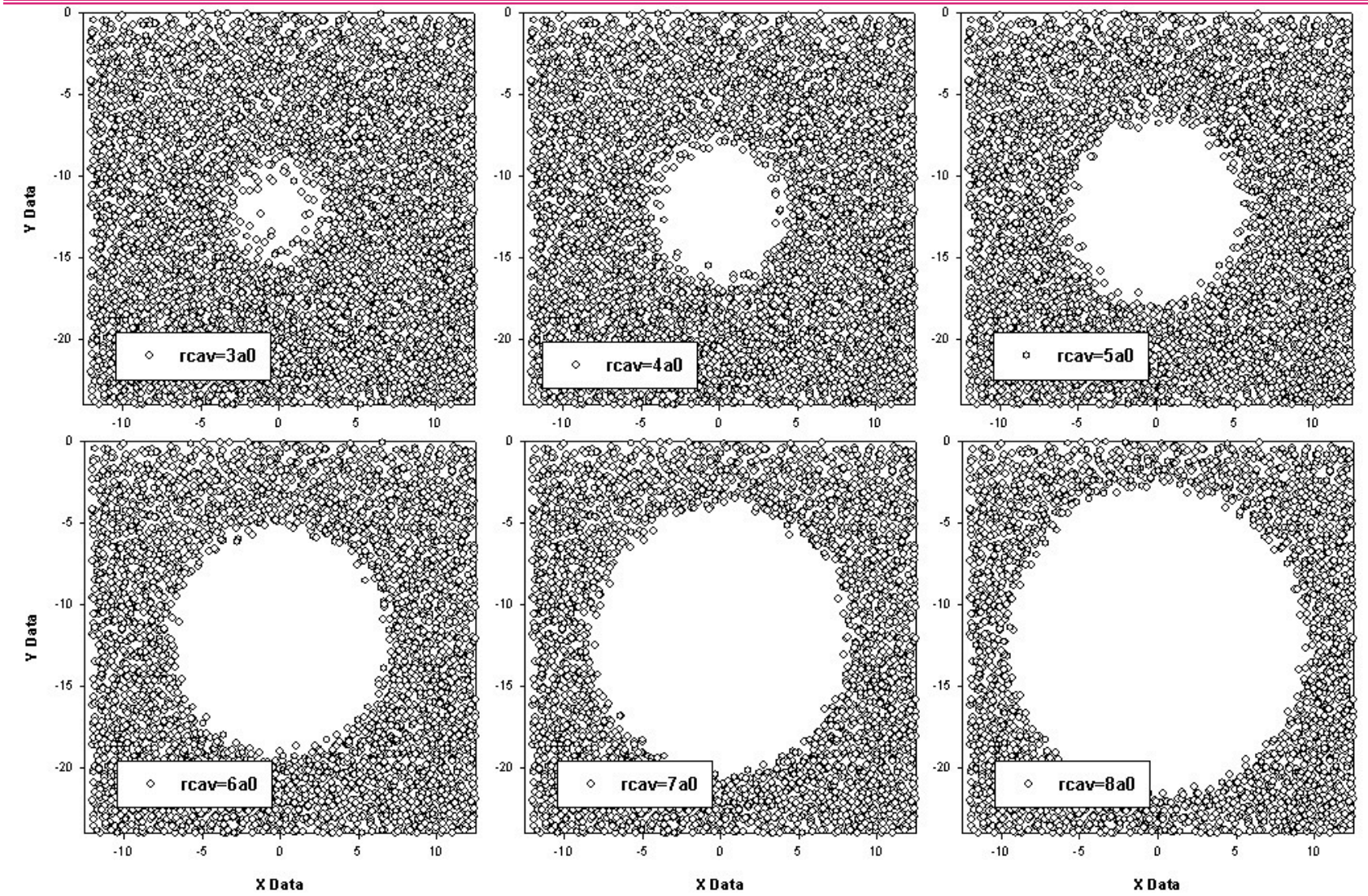


Average radial densities and pressures were calculated within a narrow spherical layers and compared with experimental data for plane surfaces (table).

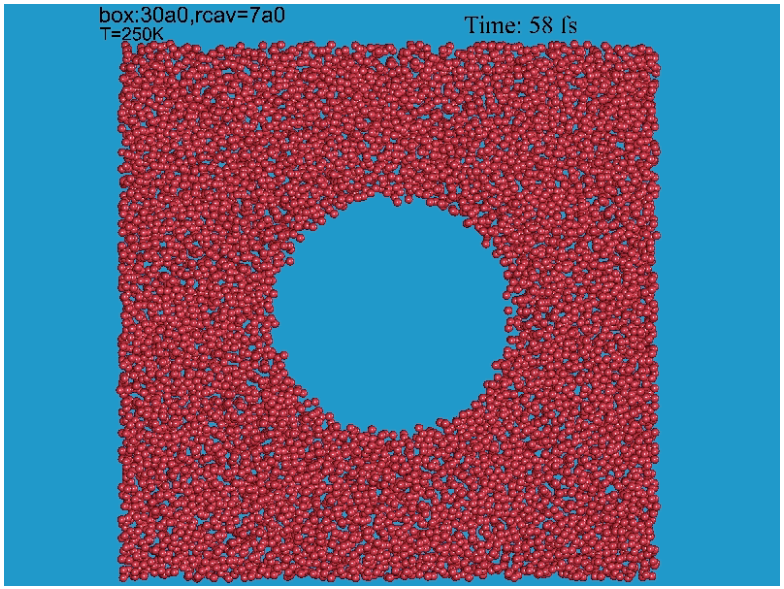
$$\left\langle \rho(r_k) \right\rangle = \left\langle \Delta N / \Delta r \right\rangle_k, k = 1 - n$$

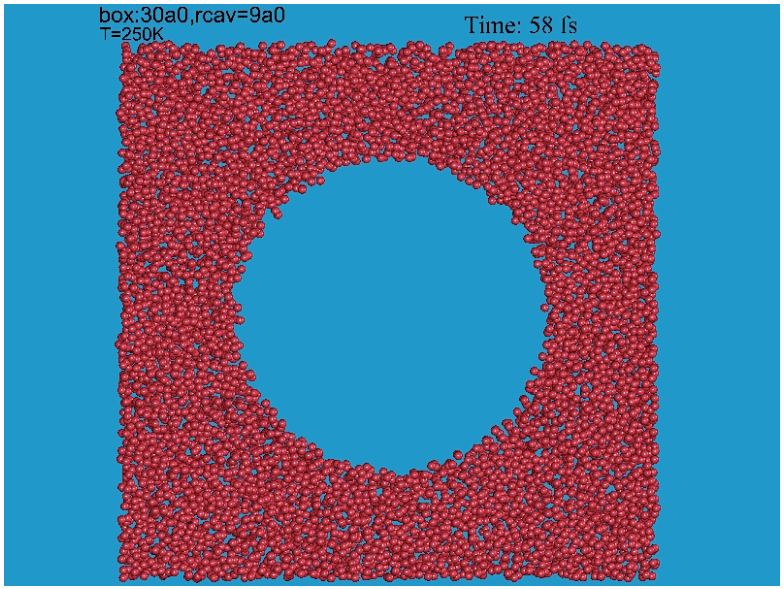
Metal	g, mN/m	g, [e/s2]	g, [eV/A]
Hg	500	0.264	2.226
Ga	750	0.396	3.339
In	550	0.290	2.448
K	100	0.053	0.445
Li	398	0.210	1.772

Surface tension of cavity in Li

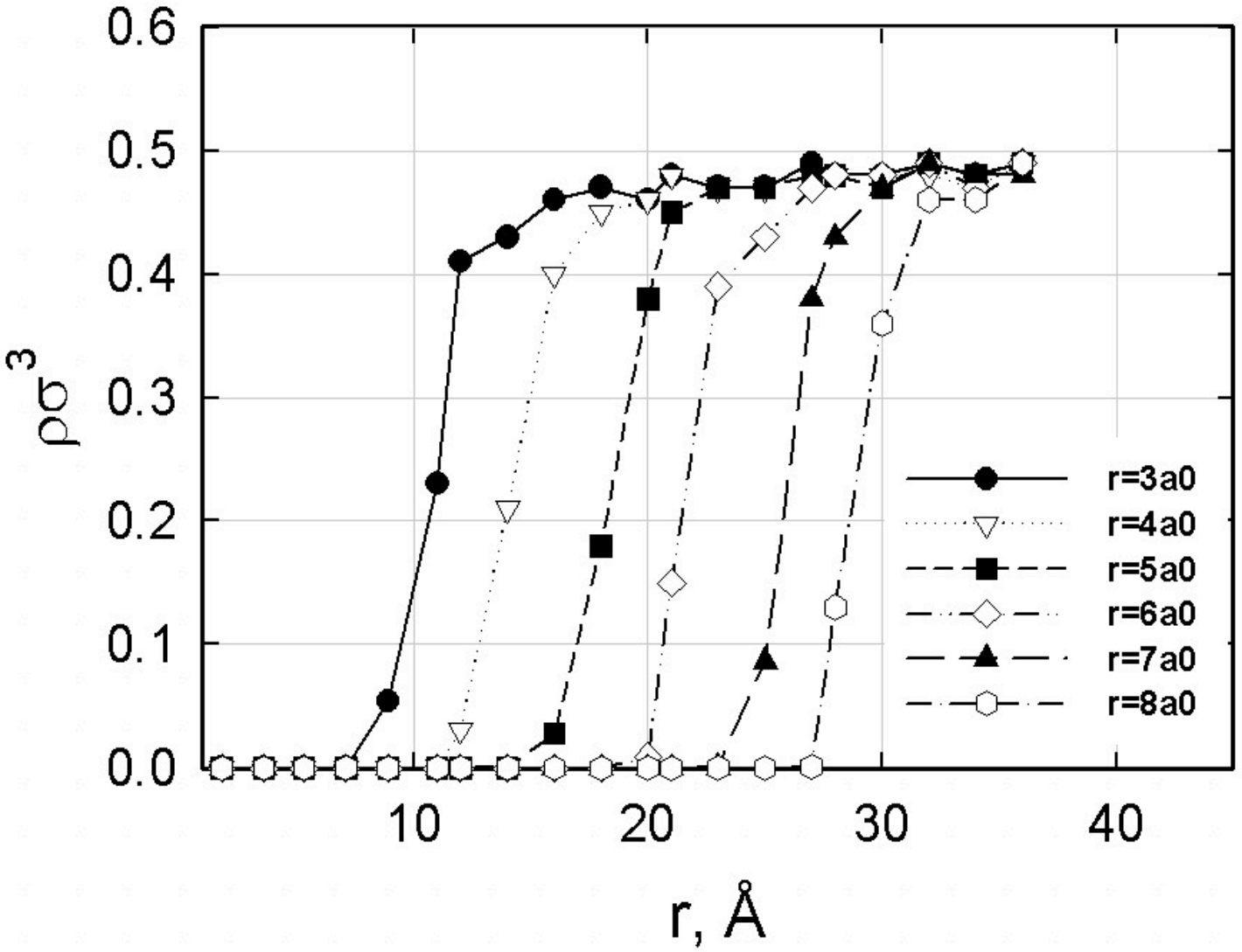


Cavity dynamics

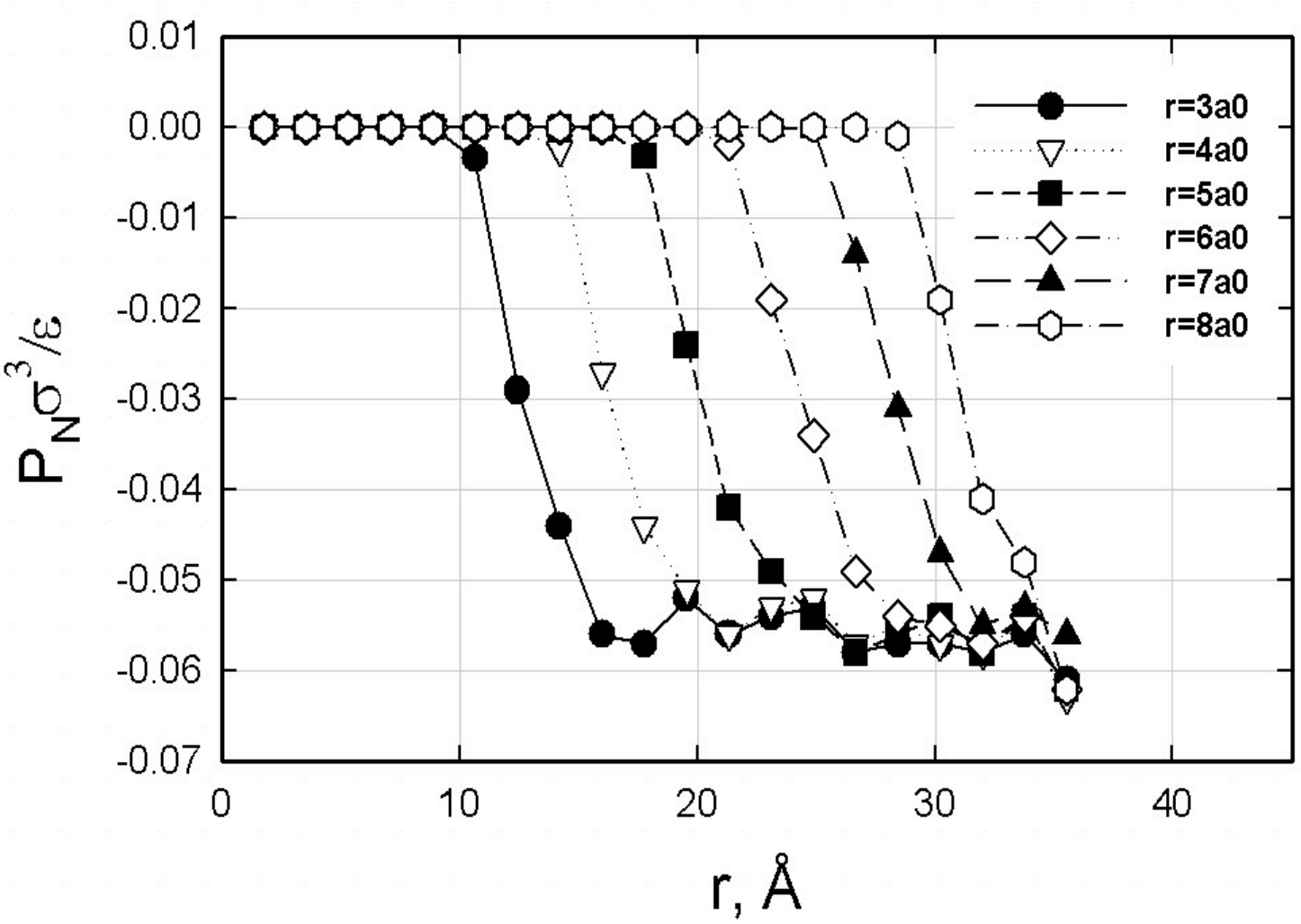




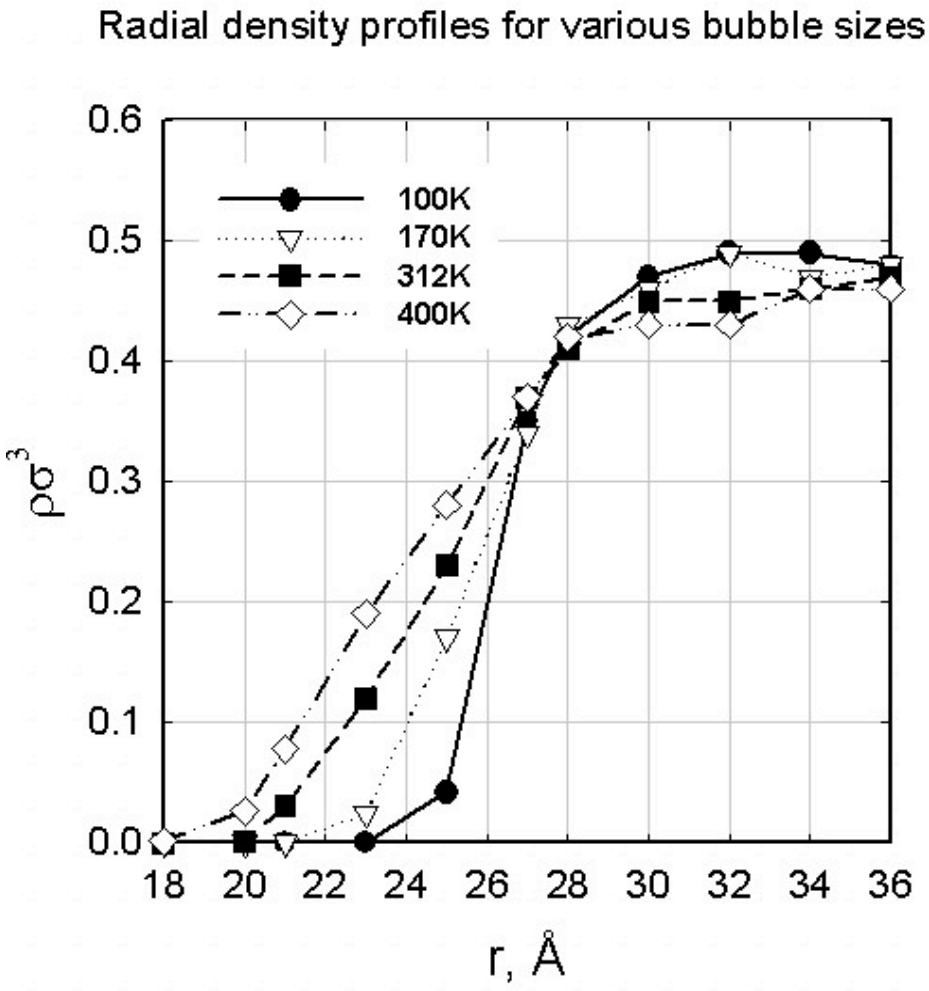
Radial density around cavities in liquid Li

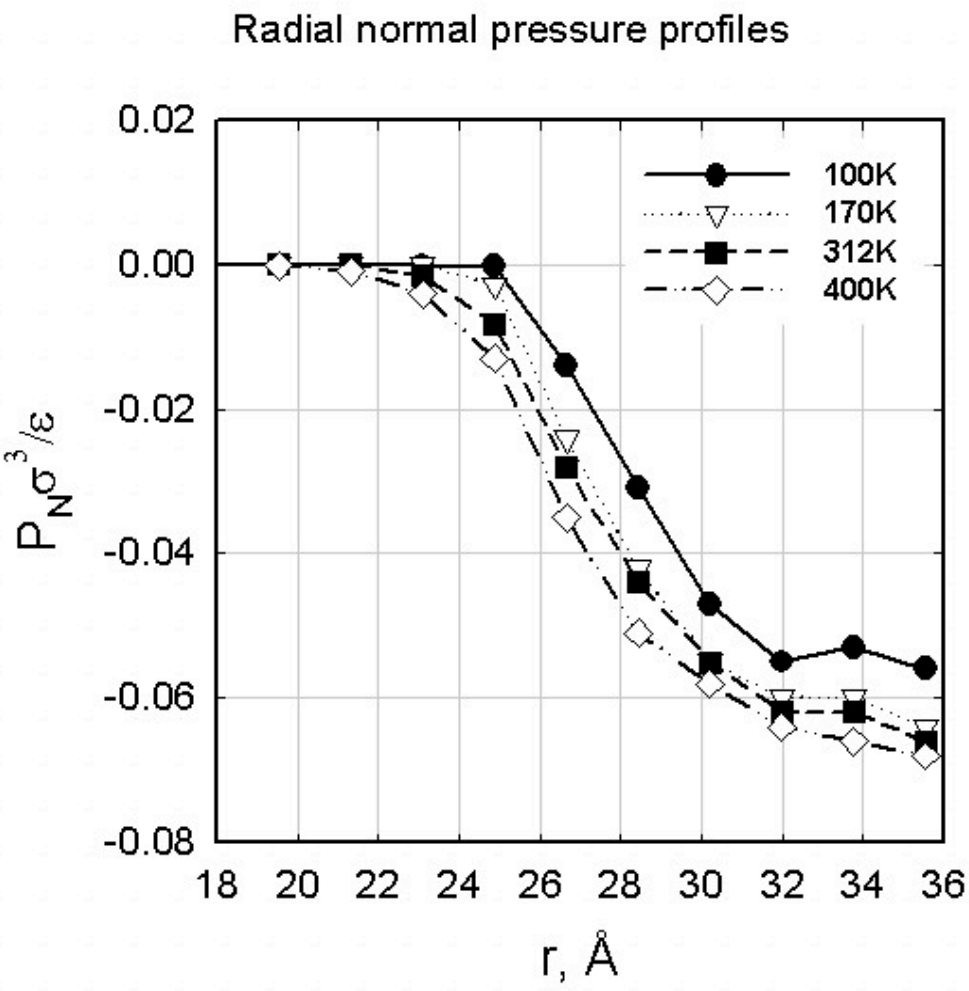


Normal pressure in liquid Li

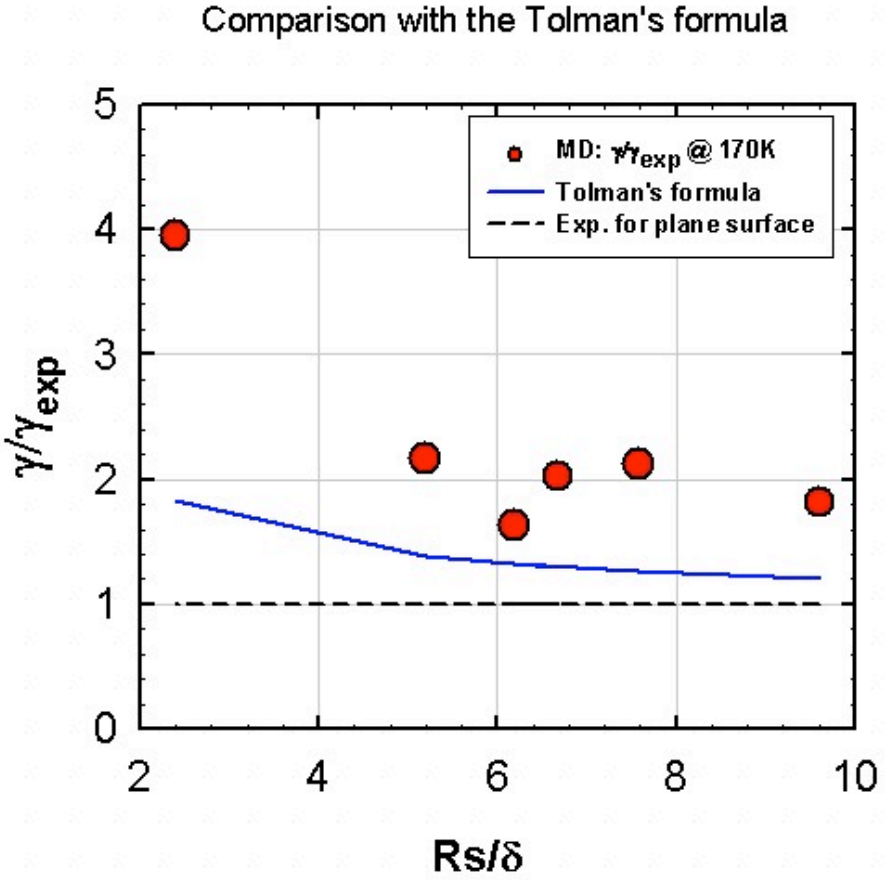


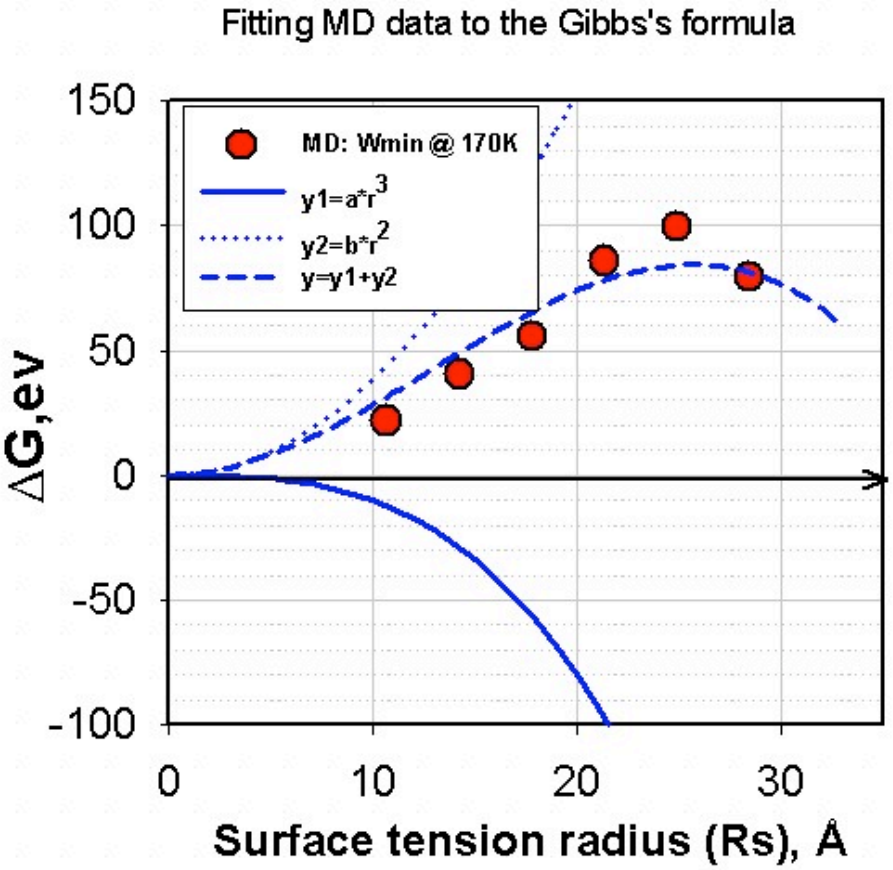
Temperature dependence of ρ, P_N



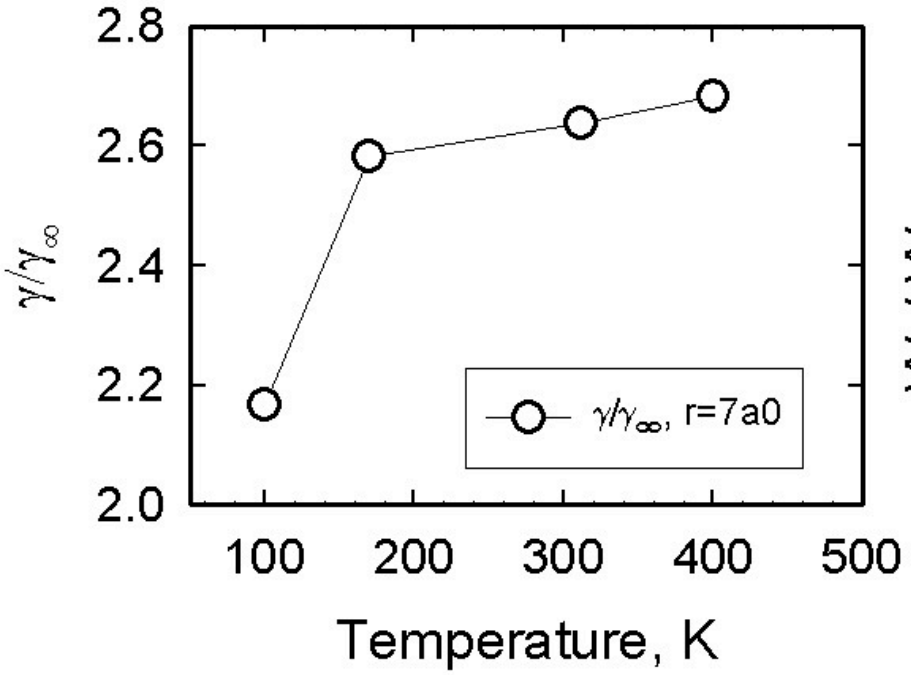


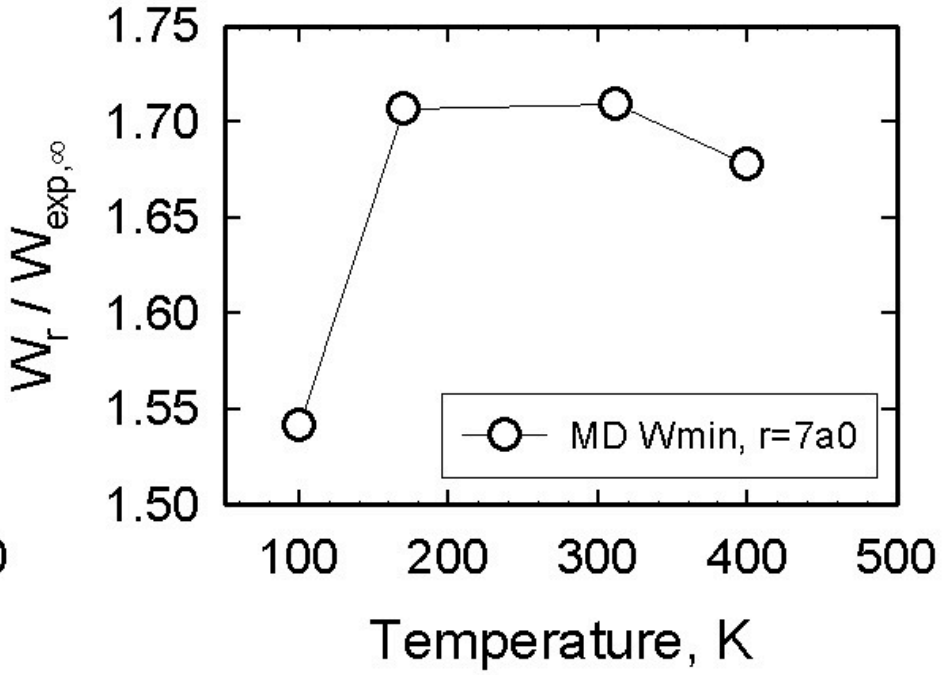
Tolman's formula and Gibbs energy





Temperature dependence of g, Wmin





$$W_{\exp} = \frac{4\pi}{3} R_S^{\,3} \cdot \gamma_\infty$$

Summary

- The new H-Li potential was tested by calculating the diffusion constants of H,D, and Tr in liquid Li and our results show that the tritium data agree well with experiment of Buxbaum & Johnson, 1985.
- Formation of small Hydrogen clusters was observed by this MD study for the first time. The relative amount of dimers is >10% at 480K.
- H, D, Tr/Li sputtering yield was calculated for the ions energy interval 10-300eV. At an energy below 50eV, the MD data are 3-10 times larger than the SRIM results.
- Cavity formation in liquid Li was studied by MD. Surface tension of small cavities was found to be larger than the experimental value for the plane surface by a factor of 2-3.
- Free energy of cavity formation in liquid lithium was calculated for a few cavity radii and they show that the cavity formation is allowed by thermodynamics.